

PATENT SPECIFICATION

(11)

1 389 732

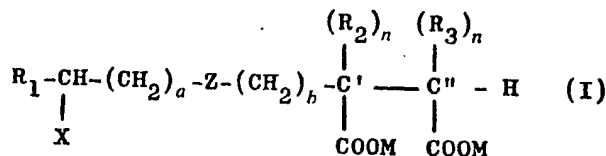
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- (21) Application 19830/72 (22) Filed 28 April 1972
 (31) Convention Application No. 139 225 (32) Filed 30 April 1971 in (19)
 (33) United States of America (US)
 (44) Complete Specification published 9 April 1975
 (51) INT CL² C11D 3/60; C07C 59/22, 65/00; (C11D 3/60, 3/20, 3/26, 3/34)
 (52) Index at acceptance
 C2C 200 20Y 220 226 227 22Y 292 29Y 304 30Y 322 323
 32Y 360 361 362 364 366 367 36Y 373 37X 394
 39Y 43X 49X 552 620 623 624 643 648 658 771
 796 79Y BU CV CW LU QU RK
 C5D 6A5D2 6A5E 6B12A 6B12B1 6B12G2A 6B12G6
 6B12N1 6B1 6B2 6C6 6C8
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(54) DETERGENT COMPOSITIONS

- (71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to detergent compositions and in particular to detergency builder compounds for use in such compositions.
- In recent years, studies have been conducted concerning the problems of eutrophication, which can be defined as a natural process of enrichment of waters with nutrients, such as phosphorus and nitrogen, at a slow rate. Eutrophication can be detrimental, since it may cause increased algal growth and algal scums which are unaesthetic, odorous, distasteful and clog filters of treatment plants. It has been postulated that various human activities have accelerated the process. Contributing factors in the eutrophication of lakes, streams and estuaries are natural run-off, agricultural drainage, ground water, precipitation, sewage and waste effluents. It has been postulated that the phosphorus-containing detergency builders present in conventional detergent compositions can be a factor in eutrophication, and therefore any substitutes which do not contain phosphorus may decrease to some extent the eutrophication problem. Thus, those skilled in the art have expended a great deal of time and money to find suitable materials to replace partially or completely the existing phosphate builders in detergent compositions.
- According to the present invention a detergent composition comprises a water soluble organic, anionic, nonionic, zwitterionic or amphoteric detergent active compound or a mixture thereof and a detergency builder having the general formula:



- wherein R₁ is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a carboxyl group (—COOM) or b phenyl group; n is zero or 1; when n is 1, R₂ and R₃ are the same or different and are hydrogen atoms, methyl groups or carboxymethyl groups (—CH₂COOM); when n is zero, a double bond is present between carbon atoms C' and C''; X is a carboxyl group (—COOM), a sulphate group (—OSO₃M) or a sulphonate group (—SO₃M); a is zero, 1 or 2; b is zero or 1; Z is a bivalent linking group —O—, —S—, —NH— or —NR₄— wherein R₄ is an alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms or a carboxy methyl group (—CH₂COOM), provided that when Z is —O—, a must be zero, X must be a carboxyl group (—COOM) and R₁ cannot be a hydrogen atom when R₂ and R₃ are hydrogen atoms and b is zero, and M is an alkali metal, an ammonium or a substituted ammonium

cation. The substituted ammonium cations are well known to the art and are for example represented by morpholinium, alkyl ammonium, mono-, di-, and trialkanol ammonium and tetra-alkyl ammonium cations. Of course if no nitrogen is desired in the detergency builder compound, the alkali metal cations should be used.

Examples of specific detergency builders which can be used in accordance with the invention are shown in Table I below, in terms of the substituent groups in formula (I) above.

TABLE I

Detergency Builder Compound

	R_1	X	Substituent groups in formula (I)					R_4
			a	Z	b	R_2	R_3	
1.	Trisodium Lactoxysuccinate $\begin{array}{c} \text{CH}_3\text{CH} - \text{O} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	COOM	0	Oxy.	0	H	H	-
2.	Trisodium 2-Gluconoxysuccinate $\begin{array}{c} \text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH} \\ \quad \quad \quad \\ \text{CH} - \text{O} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	COOM	0	Oxy.	0	H	H	-
3.	Trisodium Carboxymethylthio-succinate $\begin{array}{c} \text{CH}_2 - \text{S} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	COOM	0	S	0	H	H	-
4.	Trisodium Carboxymethylamino-succinate $\begin{array}{c} \text{CH}_2 - \text{NH} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	COOM	0	NH	0	H	H	-

TABLE I (Cont./...)

Detergency Builder CompoundSubstituent Groups in Formula (I)

	<u>R₁</u>	<u>X</u>	<u>a</u>	<u>Z</u>	<u>b</u>	<u>R₂</u>	<u>R₃</u>	<u>C' & C"</u>	<u>R₄</u>
	H	COOM	0	NR ₄	0	H	H	"	CH ₃
5. Trisodium Sarcosinylsuccinate									
$ \begin{array}{c} \text{CH}_2 - \text{N} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{CH}_3 - \text{COONa} \quad \text{COONa} \end{array} $									
6. Trisodium N-(2-carboxyethyl) aspartate									
$ \begin{array}{c} \text{CH}_2\text{CH}_2\text{NECH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array} $	H	COOM	1	NH	0	H	H	Single bond	-
7. Trisodium N-(2-sulfoethyl) aspartate									
$ \begin{array}{c} \text{NaO}_3\text{S}-\text{CH}_2\text{CH}_2\text{NECH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \end{array} $	H	SO ₃ M	1	NH	0	H	H	"	-
8. Trisodium carboxymethyloxymaleate									
$ \begin{array}{c} \text{CH}_2 - \text{O} - \text{C} = \text{CH} \\ \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array} $	H	COOM	0	Oxy.	0	-	-	Double bond	-
9. Tetrasodium α-carboxymethyloxy-β-carboxymethylsuccinate									
$ \begin{array}{c} \text{CH}_2 - \text{O} - \text{CH} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array} $	H	COOM	0	Oxy.	0	H	CH ₂ COOM	Single bond	-

TABLE I (Cont./..)

<u>Detergency Builder Compound</u>		<u>Substituent Groups in Formula (1)</u>									
		$\underline{R_1}$	\underline{X}	\underline{a}	\underline{Z}	\underline{b}	$\underline{R_2}$	$\underline{R_3}$	$\underline{C' \& C''}$	$\underline{R_4}$	
10.	Tetrasodium N-Bis (Carboxymethyl) aspartate $(\text{NaOOCCH}_2)_2\text{N}-\text{CH} \begin{array}{c} \text{--- CH}_2 \\ \\ \text{COONa COONa} \end{array}$	H	COOM	0	NR ₄	0	H	H	Single bond	CH ₂ COOM	
11.	Tetrasodium tartronoxysuccinate $(\text{NaOOC})_2\text{CHOCH} \begin{array}{c} \text{--- CH}_2 \\ \\ \text{COONa COONa} \end{array}$	COOM	COOM	0	Oxy.	0	H	H	"	-	
12.	Trisodium carboxymethyloxymethyl-succinate $\text{CH}_2\text{OCH}_2\text{CH} \begin{array}{c} \text{--- CH}_2 \\ \\ \text{COONa COONa COONa} \end{array}$	H	COOM	0	Oxy.	1	H	H	"	-	
13.	Trisodium α-carboxymethyloxy-β-methylsuccinate $\text{CH}_2 \text{--- O --- CH} \begin{array}{c} \text{--- CHCH}_3 \\ \\ \text{COONa COONa COONa} \end{array}$	H	COOM	0	Oxy.	0	H	CH ₃	"	-	

TABLE I (Cont./...)

Detergency Builder Compound

Detergency Builder Compound	Substituent Groups in Formula (I)									
	R_1	X	a	Z	b	R_2	R_3	$C' \text{ \& } C''$	R_4	
14. Trisodium $\left[(1\text{-carboxy) undecyl} \right]$ oxy succinate	$CH_3(CH_2)_9$	COOM	0	Oxy.	0	H	H	Single bond	-	
	$CH_3(CH_2)_9 \begin{array}{c} CH \\ \\ COONa \end{array} - O - CH - \begin{array}{c} CH_2 \\ \\ COONa \end{array} COONa$									
15. Trisodium N(3-carboxypropyl) aspartate	H	COOM	2	NH	0	H	H	"	-	
	$CH_2 - (CH_2)_2 - NH - CH - \begin{array}{c} CH_2 \\ \\ COONa \end{array} COONa$									
16. Trisodium N(2-hydroxyethyl)-N-carboxymethylaspartate	H	COOM	0	NR ₄	0	H	H	"	CH_2-CH_2OH	
	CH_2CH_2OH $CH_2 - N - CH - \begin{array}{c} CH_2 \\ \\ COONa \end{array} COONa$									
17. Trisodium mandeloxysuccinate	C_6H_5	COOM	0	Oxy.	0	H	H	Single bond	-	
	$C_6H_5 - CH - O - CH - \begin{array}{c} CH_2 \\ \\ COONa \end{array} COONa$									
18. Trisodium N(2-sulfoethoxyethyl)aspartate	H	OSO ₃ M	1	NH	0	H	H	"	-	
	$CH_2CH_2NH - CH - \begin{array}{c} CH_2 \\ \\ OSO_3Na \end{array} COONa$									

The major portion of the detergency builder compounds of the present invention are novel compounds, but some of the compounds have to our knowledge been suggested in the prior art, namely carboxymethylthiosuccinic acid described in The Journal of Organic Chemistry Vol. 27 pages 3140-6 (1962) authored by Zienty et al, carboxymethyloxymethylsuccinic acid described in The Chemical Abstracts Vol. 49 page 4638 (f) (1955), N-carboxymethyl and N,N-bis(carboxymethyl) aspartic acids described in Chemical Abstracts, Vol. 50 page 1450e, N- β -carboxyethyl aspartic acids described in Chemical Abstracts, Vol. 50, page 11356f, and β -carboxymethyl thio-tricarballic acid as described in U.S. patent 2,797,231. However, none of these compounds has been suggested as a detergency builder for use in a detergent composition.

Thus the invention includes the novel compounds of formula I above, provided that when Z is $-\text{S}-$ and a and b are zero, R_2 cannot be a hydrogen atom or a carboxymethyl group when R_1 and R_3 are hydrogen atoms; and when Z is $-\text{NH}-$ or $-\text{N}(\text{CH}_2\text{COOH})-$ and a and b are zero R_1 cannot be a hydrogen atom when R_2 and R_3 are hydrogen atoms. The preferred compounds are those wherein (referring to formula I above), R_1 is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms or a carboxyl group ($-\text{COOM}$); R_2 and R_3 are hydrogen atoms, methyl groups or carboxymethyl groups; X is a carboxyl group ($-\text{COOM}$); a and b are zero and Z is $-\text{O}-$, provided that both R_2 and R_3 may not be hydrogen atoms.

The detergent compositions essentially include one or more anionic, nonionic, amphoteric or zwitterionic detergent active compounds, or mixtures thereof, in addition to the detergency builders.

The synthetic detergent active compounds which can be used in the compositions of the invention are preferably anionic detergent active compounds, which are readily available and relatively cheap, and mixtures thereof. These compounds are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of such synthetic anionic detergent active compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher ($\text{C}_{10}-\text{C}_{18}$) alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl ($\text{C}_{10}-\text{C}_{18}$) benzene sulphonates, particularly sodium linear secondary alkyl ($\text{C}_{10}-\text{C}_{18}$) benzene sulphonates; sodium alkyl glyceryl ether sulphonates, especially those ethers of the higher

alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher ($\text{C}_{10}-\text{C}_{18}$) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products, the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to cover the material made by reacting olefins, particularly alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product.

If desired, nonionic detergent active compounds may also be used. Examples include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{12}) phenols, generally 5 to 25 EO; i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent active compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulfoxides.

Mixtures of detergent active compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly to impart thereto controlled low sudsing properties. This is particularly beneficial for compositions intended for use in suds-intollerant automatic washing machines. Mixtures of amine oxides and ethoxylated nonionic compounds can also be beneficial.

Many suitable detergent active compounds are commercially available and are described in the literature, for example in "Surface Active Agents and Detergents" by Schwartz, Perry and Berch.

Amounts of amphoteric or zwitterionic detergent active compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or zwitterionic detergent active compounds are used it is generally in small amounts in compositions based on the much more commonly used anionic or nonionic detergent active compounds.

The amount of the synthetic detergent active compound or compounds used is generally in the range of from about 10% to 50%, preferably about 15% to 30%, by weight of

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the composition depending on the desired properties.

5 The ratio by weight of the detergency builder compounds of the present invention to the detergent active compounds, when used in laundering and hand dishwashing compositions, ranges generally from 1:20 to 20:1, preferably 1:3 to 10:1, especially from 1:1 to 5:1. However, when the detergency builders are used in mechanical dishwashing compositions, the ratio of the detergency builder to detergent active compound is generally from 10:1 to 50:1, as much smaller amounts of the detergent active compound are then usually employed.

10 The detergency builder compounds of the present invention can be used either as the sole detergency builders or where desired they can be used in conjunction with other detergency builders, examples of which include tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphate, trisodium and tripotassium nitrilotriacetate, ether polycarboxylates, citrates, oxidised starch and cellulose derivatives, especially those containing dicarboxyl units, sodium alkenyl (C_{10} — C_{20}) succinates, sodium sulpho-fatty acids, alkali metal carbonates and orthophosphates and polyelectrolyte builders such as sodium polyacrylate and sodium copolyethylene-maleate.

15 Other conventional materials may be present in the detergent compositions of the invention, for example soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, abrasives, optical brighteners, enzymes, suds boosters, suds depressants, germicides, anti-tarnishing agents, cationic detergents, fabric softening agents, chlorine-releasing agents, oxygen-liberating bleaches such as sodium perborate with or without peracid precursors, buffers and the like. The balance of the detergent compositions is water, for example in the range of from about 5 to 15% in the powdered detergent compositions.

20 The detergent compositions of the present invention may be in any of the usual physical forms for such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes, and the like. The detergent compositions are prepared and utilised in the conventional manner, for example in the case of powdered detergent compositions they may be made by spray-drying aqueous slurries of the detergent ingredients or by dry-mixing processes.

25 When using the detergent compositions of the invention to wash clothes, the wash solutions should have a pH from about 7 to about 12, preferably from about 9 to 11. Therefore, the presence of a pH buffer in the detergent composition is usually desirable. Examples of such pH buffers are sodium silicate, carbonate and bicarbonate.

30 When the pH value of the wash solution is

below about 8.6 some of the salts of the detergency builder compounds will be present in the acid salt form and some in the normal salt form. In this connection it may also be mentioned that when the detergency builder compounds of the present invention are employed as the free acids or as partly neutralised salts, the compounds have utility in metal cleaning compositions at a pH of about 2 to about 5.

35 The invention includes a method for preparing the detergency builder compounds of the present invention. In this method a compound containing both an active hydrogen function, for example an —OH, —SH or —NH₂ group, and a salt-forming radical, for example a —COOH, —OSO₃H or —SO₃H group, is firstly reacted with an α,β -unsaturated polycarboxylic acid, to form a mixed alkaline earth metal or zinc salt, preferably the calcium salt, though other polyvalent salts can be used such as the magnesium, strontium, barium, iron, manganese and cobalt salts. The reaction is carried out in an aqueous medium having a pH of from 8 to 12.5 and preferably pH 11 to 12. The pH of the aqueous medium should be adjusted with an alkaline earth metal reagent such as calcium hydroxide, strontium hydroxide and barium hydroxide, or the corresponding oxides. If desired, an alkali metal hydroxide can be used to adjust the pH of the medium provided the alkaline earth metal reagent is also present. The mixed salt is then heated to form a reaction mixture containing a zinc or alkaline earth metal salt of the desired compound.

40 It has been found that in this reaction process, when using relatively insoluble alkaline earth metal hydroxides such as magnesium hydroxide, the initial pH at room temperature of the reaction mixture even with an excess amount of the hydroxide is only about pH 8 to 9. However, by heating the reaction mixture at reflux temperatures or by heating at superatmospheric pressures, satisfactory yields of the desired product can be obtained.

45 The mole ratio of the reactants in the process, specifically the compound containing the active hydrogen and salt-forming radicals, hereinafter referred to as the active hydrogen compound, and the α,β -unsaturated polycarboxylic acid, hereinafter referred to as the unsaturated acid, is preferably from 1:1 to 2:1. The concentrations of the active hydrogen compound and the unsaturated acid are not critical to the invention, although it is preferred to use concentrations from 0.5 molar to 5 molar in the mixed salt species. It has been found that the use of higher concentrations increases the rate of reaction.

50 The temperature at which the reactions to form the detergency builder compounds may be carried out is normal reflux temperature (100—102°C) or below reflux temperature from, say, 60°C. However, if the reaction is carried out at temperatures above reflux

temperature, is from 102° to 200°C, the rate of reaction increased so that at certain elevated temperatures the reaction may be completed within a very short time.

While the entire mechanism of the reaction is not completely understood it is believed that the reaction involves an intramolecular base-catalysed Michael-type reaction. However, the present reaction differs from the Michael reaction in that the present reaction involves intramolecular addition of a nucleophilic species across an α,β -unsaturated system. The Michael reaction is generally an intermolecular reaction which involves a carbanion and is usually carried out in anhydrous organic solvents. Also the present reaction is believed to involve alkoxide ions, mercaptide ions or amine groups and is carried out in an aqueous medium.

The mixed polyvalent salt is believed to be critical to the reaction in that it brings and holds the reacting sites of the compounds in close proximity to achieve an intramolecular addition. In fact, when the active hydrogen function is hydroxyl, the reaction does not occur in aqueous solutions at all in the absence of a polyvalent metal ion, even at high pH.

An interesting intermediate product formed during the process is the polyvalent chelate salt of the reaction product. This salt can involve either two or more molecules of the reaction product and generally can be readily isolated from the reaction mixture because of its low solubility. In some cases the polyvalent chelate salt of the reaction product is very soluble, such as in the case of lactoxysuccinate. In this case, if it is desirable to isolate the polyvalent salt, standard methods such as precipitation with an organic solvent such as ethanol, methanol or acetone is used. The conventional monochelate salt involving only one molecule of the reaction product which is soluble, may be obtained by either partially or totally cation-exchanging the chelate salt with protons followed by neutralisation with the appropriate polyvalent metal hydroxide or polyvalent metal hydroxide and alkali metal hydroxide. Examples of the polyvalent salts are monosodium calcium lactoxysuccinate, calcium hydrogen lactoxysuccinate and tricalcium bis(lactoxysuccinate).

It is to be understood that the particular cation used in the reaction will determine the particular polyvalent metal chelate salt formed. The reaction mixture is optionally treated in order to substitute hydrogen atoms, alkali metal, ammonium or substituted ammonium cations for the zinc or alkaline earth metal cations in the compounds.

The calcium chelate salts have utility as an animal feed, plant nutrient or in any other area requiring calcium. Of course, other alkaline earth metal salts and other polyvalent salts such as zinc, iron, manganese, cobalt and

the like could also be formed and used for the same or similar purposes.

While the alkali metal, ammonium and substituted ammonium salts of the detergency builder compounds of the invention are useful as builders, they are also effective as boiler scale removers, degreasers, grease cutters and rust and stain removers.

The invention is illustrated by the following Examples in which parts and percentages are by weight except where otherwise indicated.

Examples 1 to 17.

General Reaction Procedure.

An α,β -unsaturated carboxylic acid (0.20 mole) is dissolved in water (200 ml.). If the α,β -unsaturated carboxylic acid is in the anhydride form, the mixture is stirred for 10—15 minutes to convert the anhydride to the acid. Then 0.20 to 0.24 mole of the active hydrogen compound containing a salt-forming radical, preferably in its acid form, is added to neutralise all acidic groups and bring the pH to about 8—12.5 as measured initially at room temperature. The reaction mixture is then refluxed from about one to eight hours (conversion to product is followed by NMR analysis of a decalcified sample of the reaction mixture). After cooling the reaction mixture to 60°C, 10% excess sodium carbonate (based on the $\text{Ca}(\text{OH})_2$ used) is added and the mixture stirred for 10—15 minutes. The precipitated calcium carbonate is filtered and the filtrate, after adjustment of pH to 8.6 with dilute sulfuric acid or by use of a cation exchange resin, is evaporated to dryness to give the product. Analysis of the product, where possible, is carried out by NMR using an internal standard of potassium biphthalate and an external standard of tetramethylsilane. The products may be purified further, if desired, by recrystallisation from aqueous ethanol or by precipitation from water with ethanol. Excess carbonate can be removed by first acidifying, preferably with a cation exchange resin, to liberate CO_2 , followed by neutralisation to the required pH with the desired base to reform the salt which is readily isolated by filtration of the resin and evaporation of the filtrate.

When the potassium or lithium salts are desired the corresponding carbonates are used in place of sodium carbonate. When ammonium or substituted ammonium salts are desired, the product obtained from the preparation utilising an alkali metal carbonate is subsequently cation exchanged with protons followed by neutralisation with the appropriate alkaline reagent, for example ammonium hydroxide.

The compounds of Examples 1 to 17 are prepared by using the general procedure described above and show the reactants, the reflux time as well as any special reaction conditions in Table 2 below.

- However, in the case of the compound of Example 7, the general procedure was modified as follows. After refluxing the reaction mixture is filtered hot to remove insoluble calcium taurate. The filtrate was allowed to cool whereupon the pure calcium salt of the desired product precipitated out. The calcium salt was then decomposed by slurrying in water and adding 10% excess sodium carbonate (based on calcium present). The CaCO_3 was filtered off and the solution acidified by slurrying with a cation-exchange resin to decompose excess carbonate. With the ion exchange resin still present, dilute sodium hydroxide was added until the pH of the supernatant solution was 10.5. The residue was then filtered off and the filtrate evaporated to give a residue containing 88% trisodium N - (2 - sulfoethyl)aspartate (by NMR).
- For the compounds where, in the formula (I), R₁ is a substituent group other than H, and Z is —O—, such as lactoxysuccinate, the reaction time can be greatly reduced by operating the process at the higher end of the preferred pH range, say pH 12. For example, in the case of lactoxysuccinate, when the reaction was run at pH 12 and refluxed at 100°C, a reaction time of one hour was sufficient.

TABLE 2 (Cont./...)

Example	Detergency Builder Compound	Active Hydrogen/Salt Forming Radical Compound	α,β Unsaturated Carboxylic Acid or Anhydride	Reflux Time, Hours
1	Trisodium lactoxysuccinate $\begin{array}{c} \text{CH}_3\text{CH} - \text{O} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	lactic acid	maleic anhydride	7
2	Trisodium 2-Gluconoxy succinate $\begin{array}{c} \text{CH(OH)CH(OH)CH(OH)CH}_2\text{OH} \\ \quad \quad \quad \\ \text{CH} - \text{O} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	gluconic acid	maleic anhydride	5
3	Trisodium carboxymethylthio-succinate $\begin{array}{c} \text{CH}_2 - \text{S} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	mercaptoacetic acid	maleic anhydride	6

TABLE 2 (Cont./...)

Example	Detergency Builder Compound	Active Hydrogen/Salt Forming Radical Compound	α,β Unsaturated Carboxylic Acid or Anhydride	Reflux Time, Hours
4	Trisodium carboxymethylamino-succinate $\begin{array}{c} \text{CH}_2 - \text{NH} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	glycine	maleic anhydride	4
5	Trisodium Sarcosiny succinate $\begin{array}{c} \text{CH}_2 - \text{N} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{CH}_3 \quad \text{COONa} \quad \text{COONa} \end{array}$	sarcosine	maleic anhydride	4 (130°C; pressure reaction)
6	Trisodium N-(2-carboxyethyl) aspartate $\begin{array}{c} \text{CH}_2\text{CH}_2\text{NHCH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	β -alanine	maleic anhydride	7
7	Trisodium N-(2-sulfoethyl) aspartate $\begin{array}{c} \text{NaO}_3\text{S}-\text{CH}_2\text{CH}_2\text{NHCH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	taurine	maleic anhydride	8
8	Trisodium carboxymethylmaleate $\begin{array}{c} \text{CH}_2 - \text{O} - \text{C} = \text{CH} \\ \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	glycolic acid	acetylene dicarboxylic acid	1.5

TABLE 2 (Cont./...)

Example	Detergency Builder Compound	Salt Forming Radical Compound	Active Hydrogen	α, β Unsaturated Carboxylic Acid or Anhydride	Reflux Time Hours
9	Tetrasodium α -carboxymethoxy- β -carboxymethylsuccinate $\begin{array}{c} \text{CH}_2\text{-O} - \text{CH} - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa} \quad \text{COONa} \end{array}$	glycolic acid		aconitic acid	5
10	Tetrasodium N-Bis (carboxymethyl) aspartate $(\text{NaOOCCH}_2)_2\text{N-CH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa}$	iminodiacetic acid		maleic anhydride	4 (150°C; pressure reaction)
11	Tetrasodium tartronoxysuccinate $(\text{NaOOC})_2\text{CHOCH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa}$	tartronic acid		maleic anhydride	11
12	Trisodium carboxymethoxymethylsuccinate $\text{CH}_2\text{OCH}_2\text{CH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \quad \text{COONa}$	glycolic acid		itaconic anhydride	8

TABLE 2 (Cont./...)

Example	Detergency Builder Compound	Active Hydrogen/Salt Forming Radical Compound	" α , β Unsaturated Carboxylic Acid or Anhydride	Reflux Time, Hours
13	Trisodium α -carboxy-methyloxy- β -methyl succinate $\begin{array}{c} \text{CH}_2 - \text{O} - \text{CH} - \text{CHCH}_3 \\ \quad \\ \text{COONa} \quad \text{COONa} \end{array}$	Glycolic acid	citraconic anhydride	4 (140°C; pressure reaction)
14	Trisodium \int (1-carboxy) undecyl \int oxysuccinate $\begin{array}{c} \text{CH}_3(\text{CH}_2)_9 \text{CH} - \text{O} - \text{CH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \end{array}$	2-hydroxydodecanoic acid	maleic anhydride	4
15	Trisodium N (3-carboxypropyl) aspartate $\begin{array}{c} \text{CH}_2 - (\text{CH}_2)_2 - \text{NH} - \text{CH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \end{array}$	γ -aminopropionic acid	maleic anhydride	4
16	Trisodium N(2-hydroxyethyl)-N-carboxymethylaspartate $\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_2 - \text{N} - \text{CH} - \text{CH}_2 \\ \quad \\ \text{COONa} \quad \text{COONa} \end{array}$	N(hydroxyethyl)glycine	maleic anhydride	4
17	Trisodium N(2-sulfatoethyl)aspartate $\begin{array}{c} \text{CH}_2\text{CH}_2\text{NH} - \text{CH} - \text{CH}_2 \\ \quad \\ \text{OSO}_3\text{Na} \quad \text{COONa} \end{array}$	2-aminoethylsulfuric acid	maleic anhydride	4

Examples 18—33.

5 A series of detergent compositions were prepared by blending together the recited components using different detergency builder compounds of Examples 1 to 8, and the resultant compositions were then tested for detergency or cleansing ability in the Terg-O-Tometer Test. Details of the compositions and the test results are shown in Table 3 below.

10 In the detergency tests, a 65% 'Dacron'* polyester-35% cotton test cloth soiled with vacuum cleaner dust was used with water of 180 ppm hardness ions (2/1 $\text{Ca}^{++}/\text{Mg}^{++}$) at

pH 10 and at 120°F., using a product of 0.2% 15 of the total formula in the washing solution. The pH of each washing solution was adjusted, where necessary, by the addition of sodium hydroxide (NaOH) or 20 sulfuric acid thereto. The average detergency units (DU) of the compositions is the final reflectance of the washed cloth minus the initial reflectance of the soiled cloth (the average of two runs), the reflectance being measured with a Gardner Automatic Color Difference Meter, Model AC—3. 25

*'Dacron' is a Registered Trade Mark.

Table 3

Ingredient	% Ingredient in the Examples															
	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Compound of Example 1	50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Compound of Example 2	-	-	50	-	-	-	-	-	-	-	-	-	-	-	-	-
Compound of Example 3	-	-	-	-	50	-	-	-	-	-	-	-	-	-	-	-
Compound of Example 4	-	-	-	-	-	-	50	-	-	-	-	-	-	-	-	-
Compound of Example 5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Compound of Example 6	-	-	-	-	-	-	-	-	50	-	-	-	-	-	-	-
Compound of Example 7	-	-	-	-	-	-	-	-	-	-	50	-	-	-	-	-
Compound of Example 8	-	-	-	-	-	-	-	-	-	-	-	-	50	-	-	-
Sodium tripolyphosphate	-	50	-	50	-	50	-	50	-	-	-	-	-	-	50	-
Sodium silicate (SiO ₂ :Na ₂ O, 2.4:1)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Sodium linear secondary alkyl(C ₁₀ -C ₁₅)benzene sulphonate	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Water	balance to 100															
Average Detergency Units (DU's)	22.1	29.4	23.1	28.9	18.7	27.0	25.6	26.8	27.4	28.7	26.3	28.4	12.6	29.1	27.2	28.8

These compositions show useful detergency building properties using the compounds of the invention, although sodium tripolyphosphate tended to give superior results under the test conditions employed. A further series of detergent compositions were prepared having the recited ingredients of Example 18, except that each of the compounds of Examples 9 to 17 inclusive were substituted in place of the compound of Example 1. Each of these detergent compositions has acceptable building properties.

When Examples 18 and 19 were repeated using for Example 18 a recrystallised sample

of trisodium lactoxysuccinate the detergency unit results were 31.1 and 31.9, respectively.

Examples 34 to 43.

Ten further detergent compositions were prepared and tested to determine the detergency building properties of trisodium lactoxysuccinate (as used in Example 18) with a variety of detergent active compounds, using comparative sodium tripolyphosphate built compositions with the same detergent active compounds. The formulations and detergency test results under the same conditions as for Examples 18 to 33 are shown in Table 4.

TABLE 4

Ingredient

% Ingredient in the Examples

	34	35	36	37	38	39	40	41	42	43
Trisodium lactoxysuccinate	50	-	50	-	50	-	50	-	50	-
Sodium tripolyphosphate	-	50	-	50	-	50	-	50	-	50
Sodium silicate (SiO ₂ :Na ₂ O, 2.4:1)	10	10	10	10	10	10	10	10	10	10
Sodium linear sec-alkyl (C ₁₀ -C ₁₅) benzene sulphonate	18	18	-	-	-	-	-	-	-	-
Sodium α-olefin (C ₁₅ -C ₁₈) sulphonate	-	-	18	18	-	-	-	-	-	-
Sodium hydroxyalkyl(C ₁₄ -C ₁₆)-N-methyl taurate	-	-	-	-	18	18	-	-	-	-
Cocodimethyl sulfopropyl betaine	-	-	-	-	-	-	18	18	-	-
Linear sec-alkyl(C ₁₁ -C ₁₅)-7EO	-	-	-	-	-	-	-	-	20	20
Water	-	-	-	-	-	-	-	-	-	-
Average Detergency Units (DU's)	22.1	18.7	13.1	14.7	11.7	13.4	17.1	18.5	21.4	21.6

← to 100 →

Further detergency compositions to the formulations of Examples 20 to 33, except that the sodium linear sec-alkyl (C_{12} — C_{18}) benzene sulphonate is replaced by a nonionic detergent active compound "Neodol" 45—11 which is an adduct of a modified OXO-type C_{12} — C_{18} alcohol with 11 moles of ethylene oxide (EO), an amphoteric detergent active compound which is sodium hydroxyalkyl (C_{12} — C_{18})-N-methyl taurate, or a zwitterionic detergent compound which is cocodimethyl sulphopropyl betaine, have detergency building properties comparable to those when the anionic detergent compound was used.

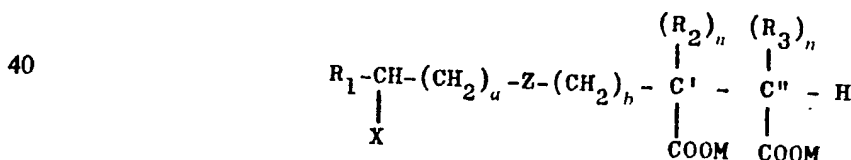
It should be appreciated that most of the compounds of the present invention form hydrates in isolatable form. For example, when crystallised from a mixture of ethanol and water, trisodium lactoxysuccinate forms a trihydrate which shows a transition peak at

135°C by Differential Thermal Analysis. Thus, when the compounds are named in the specification and in the claims, it is intended to include all hydrate forms as well as the anhydrous forms of such compounds, except in the Examples where the weights of the compounds are expressed on an anhydrous basis.

Reference is made to our copending U.K. patent application No. 55518/70 (Serial No. 1,327,115), which describes and claims carboxymethyloxysuccinate detergency builders.

WHAT WE CLAIM IS:—

1. A detergent composition comprising a water-soluble organic anionic, nonionic, zwitterionic or amphoteric detergent active compound or a mixture thereof, and a detergency builder salt having the general formula:



wherein R_1 is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a carboxyl group ($-\text{COOM}$) or a phenyl group; n is zero or 1; when n is 1, R_2 and R_3 are the same or different and are hydrogen atoms, methyl groups or carboxymethyl groups ($-\text{CH}_2\text{COOM}$); when n is zero a double bond is present between carbon atoms C' and C'' ; X is a carboxyl group ($-\text{COOM}$), a sulphate group ($-\text{OSO}_3\text{M}$) or a sulphonate group ($-\text{SO}_3\text{M}$); a is zero, 1 or 2; b is zero or 1; Z is a bivalent linking group $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$ or $-\text{NR}_4-$ wherein R_4 is an alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms or a carboxymethyl group ($-\text{CH}_2\text{COOM}$), provided that when Z is $-\text{O}-$, a must be zero, X must be a carboxyl group, ($-\text{COOM}$) and R_1 cannot be a hydrogen atom when R_2 and R_3 are hydrogen atoms and b is zero; and M is an alkali metal, ammonium or substituted ammonium cation; the weight ratio of the detergency builder salt to the detergent active compound being from 1:20 to 50:1.

2. A detergent composition according to claim 1 wherein the weight ratio of the detergent active compound to the detergency builder salt is from 3:1 to 1:10.

3. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of a carboxymethyl-oxy-maleic acid.

4. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or sub-

stituted ammonium salt of lactoxysuccinic acid.

5. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of 2-gluconoxysuccinic acid.

6. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of carboxymethyl-aminosuccinic acid.

7. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of sarcosiny succinic acid.

8. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of N(2-carboxyethyl)-aspartic acid.

9. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of carboxymethylthio-succinic acid.

10. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of N - (2 - sulfoethyl) - aspartic acid.

11. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of carboxymethyloxymethylsuccinic acid.

12. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of α -carboxymethyl-oxy- β -carboxymethylsuccinic acid.

13. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of N-bis(carboxymethyl)-aspartic acid.

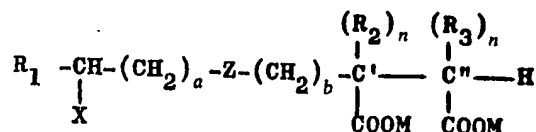
14. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or sub-

stituted ammonium salt of tartronoxysuccinic acid.

15. A detergent composition according to claim 1 or claim 2 wherein the detergency builder is an alkali metal, ammonium or substituted ammonium salt of α -carboxymethyl-oxy- β -methyl succinic acid.

16. A detergent composition according to any one of claims 1 to 15 wherein the detergency builder is used in the form of the sodium salt.

17. A compound having the general formula:



wherein R₁ is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxy-alkyl group having 1 to 4 carbon atoms, a carboxyl group (—COOM) or a phenyl group; *n* is zero or 1; when *n* is 1, R₂ and R₃ are the same or different and are hydrogen atoms, methyl groups or carboxymethyl groups (—CH₂COOM); when *n* is zero a double bond is present between carbon atoms C' and C''; X is a carboxyl group (—COOM), a sulphate group (—OSO₃M) or a sulphonate group (—SO₃M); *a* is zero, 1 or 2; *b* is zero or 1; Z is a bivalent linking group —O—, —S—, —NH— or —NR₄— wherein R₄ is an alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms or a carboxy methyl group (—CH₂COOM) and M is a hydrogen atom or a salt-forming cation; provided that when Z is —O—, *a* must be zero and X must be a carboxyl group (—COOM) and R₁ cannot be a hydrogen atom when R₂ and R₃ are hydrogen atoms; when Z is —S— and *a* and *b* are zero, R₂ cannot be a hydrogen atom or a carboxymethyl group when R₁ and R₃ are hydrogen atoms; and when Z is —NH— or —N(CH₂COOH)— and *a* and *b* are zero R₁ cannot be a hydrogen atom when R₂ and R₃ are hydrogen atoms.

18. A compound according to claim 17 wherein R₁ is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxy-alkyl group having 1 to 4 carbon atoms or a carboxyl group (—COOM); R₂ and R₃ are hydrogen atoms, methyl group or carboxymethyl groups; X is a carboxyl group (—COOM); *a* and *b* are zero; and Z is —O—, provided that both R₂ and R₃ may not be hydrogen atoms.

19. Carboxymethyloxymaleic acid or a salt thereof.

20. Lactoxysuccinic acid or a salt thereof.

21. 2-gluconoxysuccinic acid or a salt thereof.

22. Sarcosinylsuccinic acid or a salt thereof.

23. N-(2-sulfoethyl)aspartic acid or a salt thereof.

24. α - carboxymethyloxy - β - carboxymethylsuccinic acid or a salt thereof.

25. Tartronoxysuccinic acid or a salt thereof.

26. α - carboxymethyloxy - β - methylsuccinic acid or a salt thereof.

27. (1 - carboxy)undecyloxysuccinic acid or a salt thereof.

28. N - (3 - carboxypropyl)aspartic acid or a salt thereof.

29. N - (2 - hydroxyethyl) - N - carboxymethylaspartic acid or a salt thereof.

30. Mandeloxysuccinic acid or a salt thereof.

31. N - (2 - sulfatoethyl)aspartic acid or a salt thereof.

32. A carboxylic acid compound according to any of claims 17 to 31.

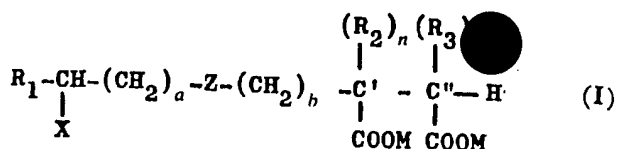
33. A compound according to any of claims 17 to 31 in the form of the alkali metal, ammonium or substituted ammonium salt.

34. A compound according to claim 33 in sodium salt form.

35. A compound according to any of claims 17 to 31 in the form of an alkaline earth metal or zinc salt.

36. A compound according to any of claims 17 to 31 in the form of the mixed sodium calcium salt.

37. A process for the preparation of a compound having the general formula:



- wherein R₁ is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a carboxyl group (—COOM) or a phenyl group; n is zero or 1; when n is 1, R₂ and R₃ are the same or different and are hydrogen atoms, methyl groups or carboxymethyl groups (—CH₂COOM); when n is zero a double bond is present between carbon atoms C' and C''; X is a carboxyl group (—COOM), a sulphate group (—OSO₃M) or a sulphonate group (—SO₃M); a is zero, 1 or 2; b is zero or 1; Z is a bivalent linking group —O—, —S—, —NH— or —NR₄— wherein R₄ is an alkyl group or a hydroxyalkyl group having 1 to 4 carbon atoms or a carboxy methyl group (—CH₂COOM) and M is a hydrogen atom or a salt-forming cation; provided that when Z is —O—, a must be zero and X must be a carboxyl group (—COOM) and R₁ cannot be a hydrogen atom when R₂ and R₃ are hydrogen atoms and b is zero, comprising the steps of:
- 25 i) forming a mixed zinc or alkaline earth metal salt of a compound containing both an active hydrogen function and a salt forming radical and an α,β-unsaturated polycarboxylic acid by reacting said compound and said unsaturated acid in an aqueous medium in the presence of a hydroxide or oxide of an alkaline earth metal or zinc or a mixture thereof at a pH of from 8.0 to 12.5 as measured at about 25°C;
 - 35 ii) heating said mixed salt to form a reaction mixture containing a zinc or alkaline earth metal salt of the desired compound of formula I above, and
 - 40 iii) optionally treating said reaction mixture in order to substitute hydrogen atoms, alkali metal, ammonium or substituted ammonium cations for the zinc or alkaline earth metal cations in the resultant compounds.
 - 45 38. A process according to claim 37 wherein heating of the mixed salts is carried out at temperatures from 102°C to 200°C.
 39. A process according to claim 37 or claim 38 wherein the reaction is conducted in the presence of calcium hydroxide.
 - 50 40. A process according to claim 37 or claim 38 wherein the reaction is conducted in the presence of calcium oxide.
 41. A process according to claim 37 substantially as described herein with reference to any of the foregoing Examples.
 - 55 42. A compound according to any one of claims 17 to 36. when prepared by a process according to any of claims 37 to 41.
 - 60 43. A detergent composition according to claim 1 substantially as described herein with reference to any of the foregoing Examples 18 to 33.

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